

ON THE TIME OF RELAXATION OF SOME ORGANIC MOLECULES IN PURE LIQUID STATE *

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ABSTRACT—The absorption of U.H.F. radio waves in the range 250-920 Mc/sec and 3.18 cm microwaves in benzyl alcohol, benzyl chloride and benzyl amine has been studied by the direct optical method by avoiding formation of stationary waves. Maximum absorption of 3.18 cm microwaves has been exhibited by benzyl alcohol, benzyl chloride and benzyl amine at temperatures 55°C, -15°C and -20°C respectively and these are assumed to be due to rotation of the substituent groups about a diameter of the benzene ring passing through the point of substitution.

In the U.H.F. region in the case of benzyl chloride peaks have been observed at 400 Mc/sec at 28°C and at 790 Mc/sec at 25°C which are due to dimers and monomers respectively. Similarly, in the case of benzyl amine a peak due to dimer at 275 Mc/sec at 25°C and a peak due to monomer at 700 Mc/sec at 0°C have been observed. In the case of benzyl alcohol absorption maxima have not been observed in this region, but indication of the existence of a maximum beyond 850 Mc/sec has been observed. The radius of the rotor in this case comes out too low to be that of the molecule. In all the cases the absorption peaks in the U.H.F. region shift with change of temperature according to Debye's theory.

The results obtained in the present investigation show that in these substituted benzenes the time of relaxation has different discrete values in each case and the occurrence of 'effective time of relaxation' postulated by Fisher is corroborated by these results.

INTRODUCTION

It was reported previously by Sen (1950), Kastha (1952) and by the present author (Ghosh, 1953a) that some substituted benzenes exhibit absorption maxima in the frequency range 250-900 Mc/sec at suitable temperatures and that the diameters of the rotors calculated from Debye's theory correspond to those of the single molecules in some cases and to those of the dimers in other cases. It was also pointed out by the present author that with lowering of temperature of the liquid associated groups of molecules are formed in the liquid state and they exhibit new absorption maxima corresponding to their times of relaxation. It was further observed by the present author (Ghosh, 1953b) that some organic liquids, such as chloroform ethylene chloride etc., absorb microwaves of wavelength 3.18 cm at suitable temperatures and the absorption becomes maximum for certain values of the temperatures of the liquids. The radius of the rotor calculated from Debye's theory in the case of ethylene chloride was found to be smaller than that of the single molecule and it was pointed out that the rotor may be one half

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EXPERIMENTAL

Fig. 1 Circuit diagram of the power supply.

was tested by noting the variation of the input voltage with the corresponding change in the output voltage. It was observed that the output voltage remained constant when the input voltage was changed from 220 to 240 volts. The output voltage was also observed to remain constant over a wide range of loads. A GR 857-A and a GR 1200-A with its shield removed was used as the source of radio waves of frequencies ranging from 250 Mc/sec to 920 Mc/sec. The liquids studied were of chemically pure quality. They were all distilled in vacuum after proper dehydration. In order to study the absorption at different temperatures the cell filled with the liquid was placed in baths at different temperatures and when the liquid attained the temperature of the bath, the cell was taken out and its outer surfaces were cleaned before being placed in the path of the waves between the oscillator and the receiver. The reading of the microammeter in the receiving circuit with the cell filled with benzene placed in a suitable position in the path of the waves was taken as the incident intensity, in all the cases. In the case of microwaves the position of the cell was adjusted till the transmission was maximum and the formation of stationary waves was avoided in this way.

RESULTS

The values of apparent absorption coefficient, μ were calculated from the relation

$$\mu = \frac{2.34}{x} \log_{10} \left(\frac{I_0}{I} \right) \quad \dots (1)$$

where x is the thickness of the liquid absorber.

The values of μ have been plotted against the temperatures in figures 2, 4 and 8 for the microwave region and the values of μ have been plotted

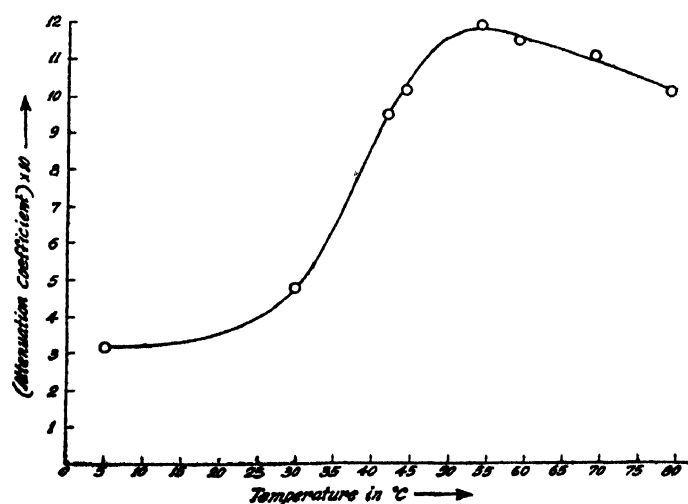


Fig. 2 Benzyl alcohol at 9413 cm. Thickness of the liquid 1 cm.

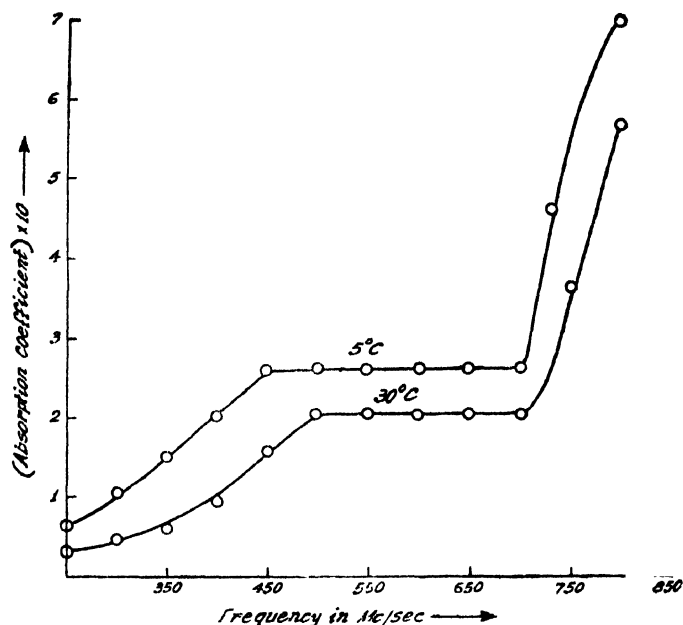


Fig. 3 Benzyl alcohol. Thickness of the liquid, 3.5 cm.

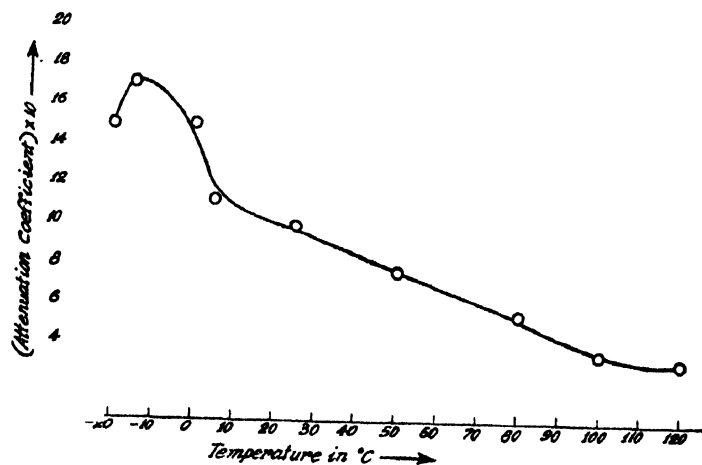


Fig. 4 Benzyl chloride at 9415 Mc/sec. Thickness of the liquid, 1 cm

against frequencies in the figures 3, 5, 6 and 7 for the U.H.F. region. Times of relaxation have been calculated from Debye's equation

$$\omega\tau = \frac{\epsilon_0 + 2}{\epsilon_1 + 2} \sqrt{\frac{\epsilon_1}{\epsilon_0}} \quad \dots (2)$$

and the values of a^3 , the cube of the radius of the rotor, have been obtained again from Debye's equation

$$a^3 = \frac{\tau k T}{4\pi\eta} \quad \dots (3)$$

The values of different constants involved in the calculation of τ and a^3 are given in Table I.

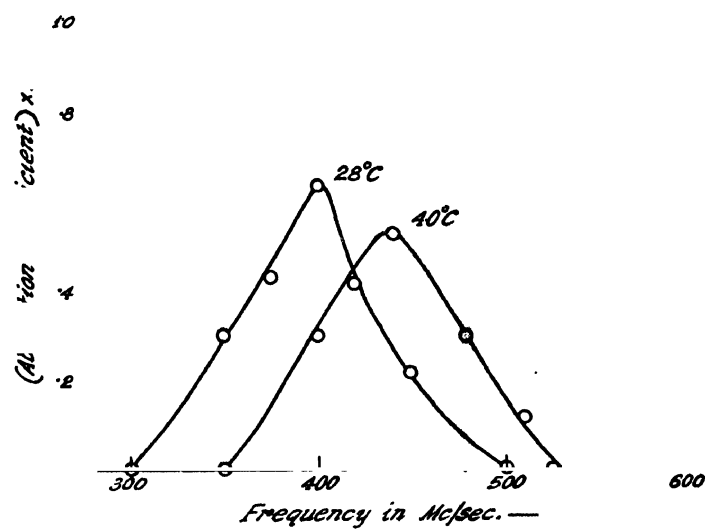


Fig. 5 Benzyl chloride. Thickness of the liquid, 3.5 cm.

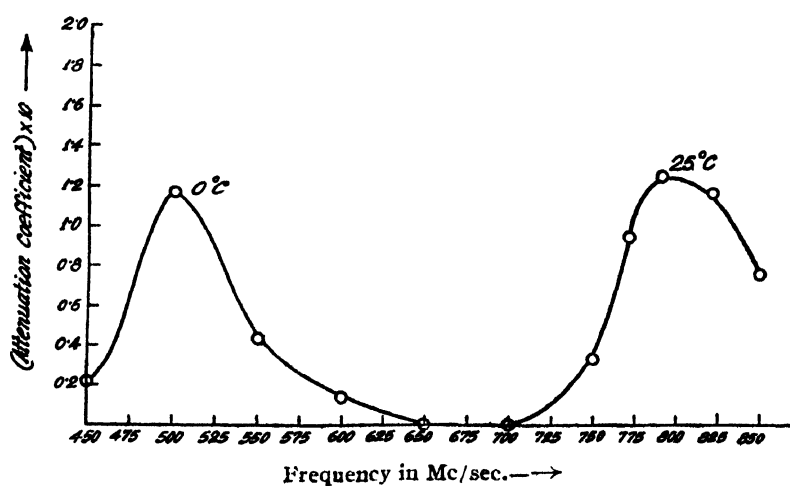


Fig. 6 Benzyl chloride. Thickness of the liquid, 3.5 cm.

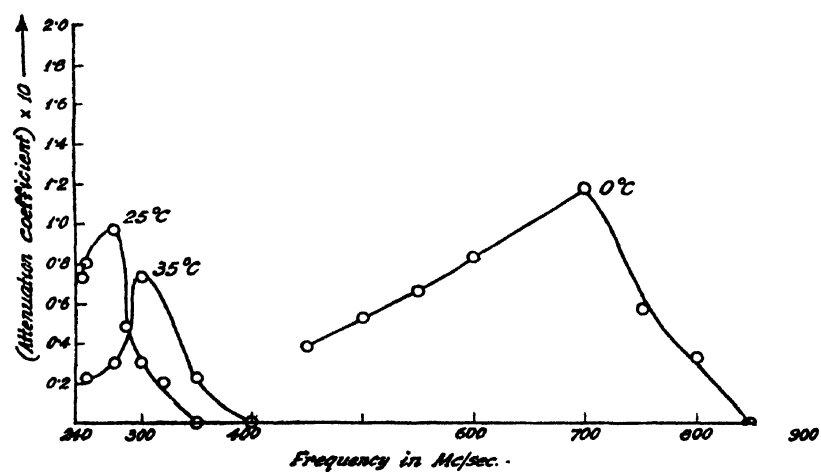


Fig. 7 Benzyl amine at 9451 Mc/sec. Thickness of the liquid 3 cm.

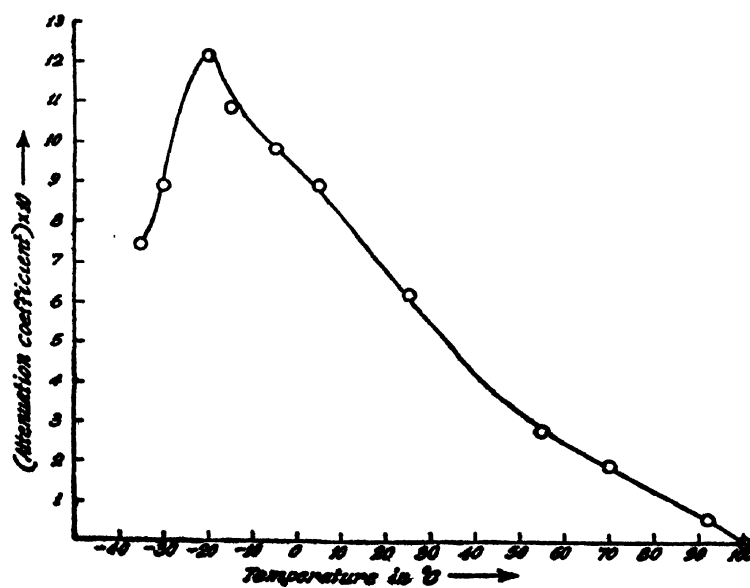


Fig. 8 Benzyl amine. Thickness of the liquid 1.5 cm.

TABLE I

Liquid	$\frac{\omega}{2\pi}$ in Mc/sec	$T^\circ\text{K}$ for max. absorption	ϵ_0	ϵ_1	$\eta \times 100$	$\tau \times 10^{11}$	$a^3 \times 10^{24} \text{c.c.}$
Benzyl alcohol	900 (aprox)	303		12.4	4.3	12.24	9.354
	9415	328	2.37	10.3	2.8	1.249	1.195
Benzyl chloride	400	301		5.75	1.2	34.76	95.04
	440	313		4.5	1	13.53	114.3
			2.371				
	500	273		8.1	1.76	25.34	42.85
	750	298		6	1.28	17.5	44.1
Benzyl amine	9415	258		9.3	1.97	1.303	1.843
	275	298		4.5	1.59	53.47	100.2
	300	308		4.45	1.18	49.15	116.6
			2.381				
	700	273		5.55	1.81	20.13	32.56
	9415	253		7	2.06	1.409	1.88

The values of η are obtained by extrapolation from the results reported in Handbook of Chemistry and Physics published by Chemical Rubber Publishing Co., the International Critical Tables and from Physico-chemical constants of pure organic compounds published by J. Timmermans (1950). The values of ϵ_1 have been obtained from the table of dielectric constants of pure liquids published by National Bureau of Standards, United States, Department of Commerce, and also from the International Critical Tables. The results at very low temperatures have been obtained by extrapolation. The values of ϵ_0 have been assumed to be equal to square of n , the refractive index at 20°C for sodium D line, because the values of n at lower temperatures were not available.

DISCUSSIONS

It can be seen from Table I that all the three liquids exhibit maximum absorption of 3.18 cm microwaves at suitable temperatures and cubes of the radii of the rotors are 1.595, 1.83 and 1.88×10^{-24} cc. in the case of benzyl alcohol, benzyl chloride and benzyl amine respectively. As the cubes of radii of the molecules are many times larger than these values, the rotors cannot be the whole molecules. The radii, however, agree to some extent with those of the circles along which the substituent groups would move if they had rotational freedom. Thus probably, these absorption maxima are due to rotation of the substituent groups about a diameter of the benzene ring passing through the carbon atom of the ring with which the substituent group is attached.

As regards the absorption in the U.H.F. region, the behaviour of benzyl alcohol is different from that of either benzyl chloride or benzyl amine.

Each of the latter two liquids shows two absorption maxima in the region between 250 Mc/sec and 900 Mc/sec. The radius of the rotor corresponding to one of the two absorption maxima lies between 3 Å and 4 Å in both these cases and that corresponding to the other maximum is about 4.8 Å. The lower value may correspond to that for a monomer and the higher value may correspond to the radius of the dimer. The agreement is fairly satisfactory in view of the fact that the values of the macroscopic viscosities have been taken in the calculation and these values have again been obtained by extrapolation. The fact that the absorption peaks both at lower and higher frequencies shift with change of temperature of the liquid as shown in figures 3, 5, 6 and 7 shows that the absorption is genuine. The change of dielectric constant which takes place with the change of temperature cannot explain the shift of the peaks if it is assumed that the apparent absorption is due to formation of stationary waves in the cell.

The results obtained in the present investigation show that in these substituent benzenes the time of relaxation has different values in each case and the occurrence of 'effective time of relaxation' postulated by Fischer (1949) is corroborated by these results. The influence of constitution of the substituents on the value of the radius of the rotor is quite evident from a comparison of the results for benzyl alcohol with those for the other two liquids. In the former case no absorption peak is observed in the range 250-900 Mc/sec and there is indication of the occurrence of a peak at a frequency higher than 850 Mc/sec. Even if the frequency is taken as 900 Mc/sec the cube of the rotor calculated from Debye's theory becomes 0.35×10^{-24} cc. This is much smaller than the corresponding values for the other two molecules. This discrepancy may be due to the fact that the macroscopic viscosity is much larger in the case of benzyl alcohol than that in the case of the other two liquids and that the viscous forces actually acting on the molecule during its orientation in the liquid are much weaker than the macroscopic viscosity as pointed out by Sirkar (1953). Probably the presence of OH groups facilitates hydrogen-bonding among neighbouring molecules increasing thereby the macroscopic viscosity, but a small percentage of single molecules still exists in the liquid and when these molecules try to orient, the forces acting on them are just ordinary viscous forces and not the forces increased in strength by hydrogen-bonding.

Investigations with other molecules of similar structure are in progress.

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